LAMONT GEOLOGICAL OBSERVATORY
COLUMBIA UNIVERSITY
PALISADES, NEW YORK

Annual Summary Report

15 December 1965 - 14 December 1966

AF-AFOSR Contract No. 49(638)-1355
ARPA Order No. 292-66 Amnd 32
ARPA Project Code No. 4810 & 3810 - Task 8652
Starting Date: 15 December 1963
Termination Date: 14 December 1966
Amount of Contract: $228,240
Principal Investigator: Dr. Orson L. Anderson
Code 914 EL 9-2900
Scientist: Dr. Edward Schreiber
Code 914 EL 9-2900
Report Written By: Dr. Edward Schreiber

"Measurement of P and S Sound Velocities
Under Pressure on Laboratory Models of
the Earth's Mantle"

ABSTRACT

The results of velocity measurements performed on specimens of polycrystalline forsterite with 6% porosity, a single crystal spinel, and on obsidian are reported. The velocities of compressional and shear waves were determined at both ambient (25°C and 1 bar) conditions and as a function of pressure on all three specimens. Velocity as a function of temperature was measured to 150°C at 1 atm on the obsidian specimen. The results are given by the following equations for the two isotropic materials (forsterite and obsidian); P is in kbars and T is in °C:

Forsterite:

$$v_p = 7.586 + 1.03 \pm 1.03 \pm 5\% \times 10^{-2}\ P$$

$$v_s = 4.359 + 2.45 \pm 5\% \times 10^{-3}\ P$$

Obsidian:

$$v_p = 5.713 - 1.87 \times 10^{-2}\ P$$

$$v_s = 3.526 - 1.43 \times 10^{-2}\ P$$

The results for the spinel are given in terms of the single crystal elastic constants:

	c_{11}	c_{12}	c_{44}	
1 bar	2985.7	1537.2	1575.8	(kbar)
2 kbar	2995.5	1545.0	1577.5	(kbar)

The isotropic bulk modulus B, Poisson's ratio σ, and the pressure derivatives of the bulk modulus (dB/dP) computed from the above are:

	B_s	dB_s/dP	σ
Forsterite	973.6 kbar	4.8	0.254
Spinel	2019.9 kbar	4.18	0.260
Obsidian	378.6 kbar	-0.87	0.192

The derivatives of the velocities and of the bulk modulus for obsidian were found to have an opposite sign from those values found for the other materials.

I. INTRODUCTION

The work performed in the period December 15, 1965, to December 14, 1966, is presented in this report. The studies carried out involved the measurement of the elastic properties and their variation with pressure. Materials included in this report are a polycrystalline forsterite, single crystal spinel, and obsidian (glass of volcanic origin). The specimen of forsterite is of a rather poor quality, having about 6% porosity. The importance of forsterite to the studies concerning the earth's mantle is such that data upon a poor specimen are useful.

The program differs from the usual experiments on the elastic properties of rock in that we perform our measurements upon specimens of sufficient quality in order to obtain as great an accuracy as possible. From these measurements we have been able to define the pressure derivatives of the elastic properties. These derivatives are used to extrapolate our data, taken at very low pressures, into the regime of very high pressures.

II. PUBLICATIONS

During this year, the following papers, which resulted from our work, have appeared or were submitted for publication:

1. "The Pressure Derivatives of the Sound Velocities of Polycrystalline Alumina," E. Schreiber and O. L. Anderson, J. Am. Ceram. Soc., 49[4], 184-190, 1966.

2. "Seismic Parameter ϕ: Computation at Very High Pressure from Laboratory Data," O. L. Anderson, Bull. Seismol. Soc. Am., 56[3], 725-731, 1966.

3. "Temperature Dependence of the Velocity Derivatives of Periclase," E. Schreiber and O. L. Anderson, J. Geophys. Res., 71[12], 3007-3012, 1966.

4. "A Variable Impedance Matching Transformer," Paul Mattaboni and E. Schreiber, Rev. Sci. Instr., 37[11], 1625-1626, 1966.

5. "Pressure Derivatives of the Sound Velocities of Polycrystalline Forsterite, with 6% Porosity," E. Schreiber and O. L. Anderson, J. Geophys. Res., in press.

6. "Elastic Moduli of Synthetic Single Crystal Spinel at 25°C and to 2 Kbar," E. Schreiber, submitted for publication.

III. MEASUREMENTS AND RESULTS

A. Polycrystalline Forsterite and Single Crystal Spinel

The results of the studies upon a specimen of polycrystalline forsterite with 6% porosity and a specimen of a single crystal spinel are reported in the attached preprints, Appendices A and B.

B. Obsidian

Velocity measurements have been performed upon a sample of obsidian up to pressures of 3 kbar at 25°C, and the pressure derivatives of the velocities and bulk modulus have been determined. The results of these measurements indicate that

the behavior of the elastic properties of obsidian differs from that which we have found for polycrystalline materials.

The specimen which we used came from Oregon, and was prepared in the usual way in the form of a cube about 1 cm on edge. The chemical analysis of this sample is given in Table I. The density, determined by Archimedes' method, was found to be 2.357 gms/cm^3.

The velocities were determined using the method of pulse superposition,[1] described in our previous reports.[2] The dependence of velocity upon pressure is calculated from the measured relative change in frequency (f/f_o) and the relative change in length (ℓ/ℓ_o) using equation (1)

$$v = v_o\ (f/f_o)\ (\ell/\ell_o) \qquad (1)$$

The ratio (ℓ/ℓ_o) is calculated from the frequency data using the equations given by Cook[3] and described in our previous reports.[2]

The adiabatic bulk modulus (B) and its pressure derivative (dB/dP) and Poisson's ratio (σ) are computed from the measured velocities using the following relations:

$$B = \rho\left(v_p{}^2 - \frac{4}{3}\, v_s{}^2\right) \qquad (2)$$

$$\frac{dB}{dP} = 2\rho\left[v_p\left(\frac{dv_p}{dP}\right) - \frac{4}{3}\left(\frac{dv_s}{dP}\right)\right] + (1+T\alpha_v\gamma) \qquad (3)$$

$$\sigma = \frac{1}{2}\left\{1 - \left[\left(\frac{v_p}{v_s}\right)^2 - 1\right]\right\}^{-1} \qquad (4)$$

TABLE I. Chemical analysis of obsidian

Constituent		Weight %
SiO_2		76.19
Al_2O_3		12.61
Fe_2O_3		0.02
FeO		0.64
MgO		0.01
CaO		0.72
Na_2O		4.84
K_2O		4.26
$H_2O(+)$		0.85
$H_2O(-)$		0.21
TiO_2		0.17
MnO		0.03
P_2O_5		0.01
	Total	100.56

Equation (3) requires the volume expansion, α_v; and the Grüneisen constant, γ. The value of $10.2 \times 10^{-6}\,^{\circ}C^{-1}$ for α_v was obtained from a measurement of the linear expansivity. A value of $\gamma = 0.15$ was obtained by first estimating the Debye temprrature from the mean sound velocity.[4] The heat capacity at constant volume was obtained from the Debye temperature[5] and the chemical composition; the Grüneisen constant was then calculated by an iteration using the equations

$$\frac{C_p}{C_v} = (1 + T\alpha_v\gamma) \tag{5}$$

$$\gamma = \frac{\alpha B_s}{C_p \rho} \tag{6}$$

The results of the measurements at the ambient conditions of 25°C and 1 bar are given in Table II.

TABLE II. Elastic properties of obsidian at 1 atm and 1 bar

Property	Symbol	Value
Longitudinal Velocity	v_p	5.713 km/sec
Shear Velocity	v_s	3.526 km/sec
Bulk Modulus	B	378.6 kbar
Poisson's Ratio	σ	0.197

Specimen density = 2.357 gms/cm^3

The variation of the frequency with pressure is shown in Figures 1 and 2. The variation of velocity was computed from these data, and can be expressed by means of the relations (P is in kbars)

$$v_p = 5.713 - 1.87 \times 10^{-2} P \tag{7}$$

$$v_s = 3.526 - 1.43 \times 10^{-2} P \tag{8}$$

The value of the pressure derivative of the bulk modulus calculated using equation (3) is dB/dP = - 0.87 kbars.

IV. DISCUSSION

The results on obsidian are of interest because the velocities are decreasing with increasing pressure. This is in agreement with the measurement of Birch[6] and Birch and Bancroft[7] upon a sample of obsidian from California. This reversal in velocity benavior also applies to the variation of the bulk modulus with pressure, which is not only much smaller than the value of 4 which we have found for crystalline solids, but is also negative. A negative value of dB/dP is in agreement with the findings of Bridgman[8] for silica-rich glasses.

V. FUTURE WORK

We plan to explore the effects of temperature upon the elastic properties of the spinel single crystal and upon the obsidian specimens. We have also arranged for the hot-pressing

of dense polycrystalline forsterite, spinel, and enstatite. Future work on these specimens is contingent upon the success of the hot-pressing effort. Although we have performed measurements upon samples of two of these materials, we believe it useful and necessary to carry out further measurements upon dense polycrystalline specimens, particularly upon the forsterite, as our present specimen contained 6% porosity.

VI. FINANCIAL STATEMENT

The financial statement at the present time is:

Estimated expenditures and commitments to date	$223,503.00
Estimated funds to completion	44,717.00
Estimated date of completion	14 December 1967

Orson L. Anderson

Orson L. Anderson

Edward Schreiber

Edward Schreiber

REFERENCES

1. McSkimin, H. J., Pulse superposition method for measuring ultrasonic waves in solids, J. Acoust. Soc. Am., 33, 12-16, (1961).
2. Anderson, O. L., and E. Schreiber, Measurement of P and S sound velocities under pressure on laboratory models of the earth's mantle, Final Report AF-AFOSR 49(638)-1355, (1965).
3. Cook, R. K., Variation of elastic constants and static strains with hydrostatic pressure; A method for calculation from ultrasonic measurements, J. Acoust. Soc. Am., 29[4], 445-448, (1957).
4. Anderson, O. L., A simplified method of calculating the ebye temperature from elastic constants, J. Phys. Chem. Solids, 24, 909-917, (1963).
5. Furukawa, G. T., and T. B. Douglas, American Institute of Physics Handbook, (McGraw-Hill Book Company, New York, 1957), 2nd ed., Ch. 4e.
6. Birch, F., The velocities of compressional waves in rocks to 10 kilobars, Part 1, J. Geophys. Res., 65[4], 1083-1102,(1960).
7. Birch, F., and D. Bancroft, The effect of pressure on the rigidity of rocks. 1., J. Geol., 46[1], 59-87, (1938).
8. Bridgman, P. W., The compression of 39 substances to 100,000 kg/cm^2, Proc. Am. Acad. Arts Sci., 76, 55-70, (1948).

FIGURE CAPTIONS

Figure 1 Frequency versus pressure: Shear mode in obsidian.

Figure 2 Frequency versus pressure: Longitudinal mode in obsidian.

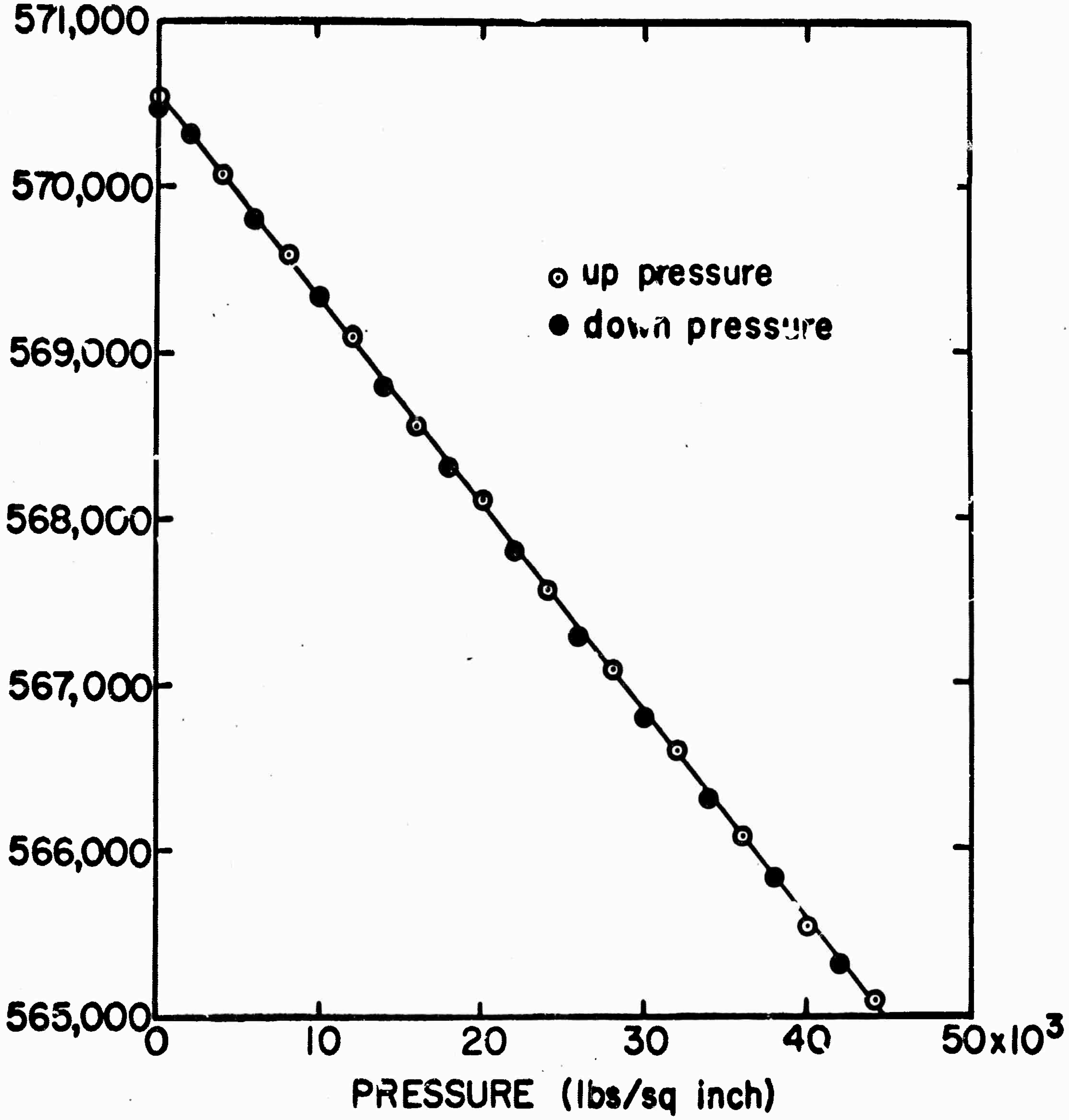
571,000
570,000
569,000
568,000
567,000
566,000
565,000
FREQUENCY (cycles/sec)
0
10
20
30
40
50x10³
PRESSURE (lbs/sq inch)
up pressure
down pressure

Fig. 1

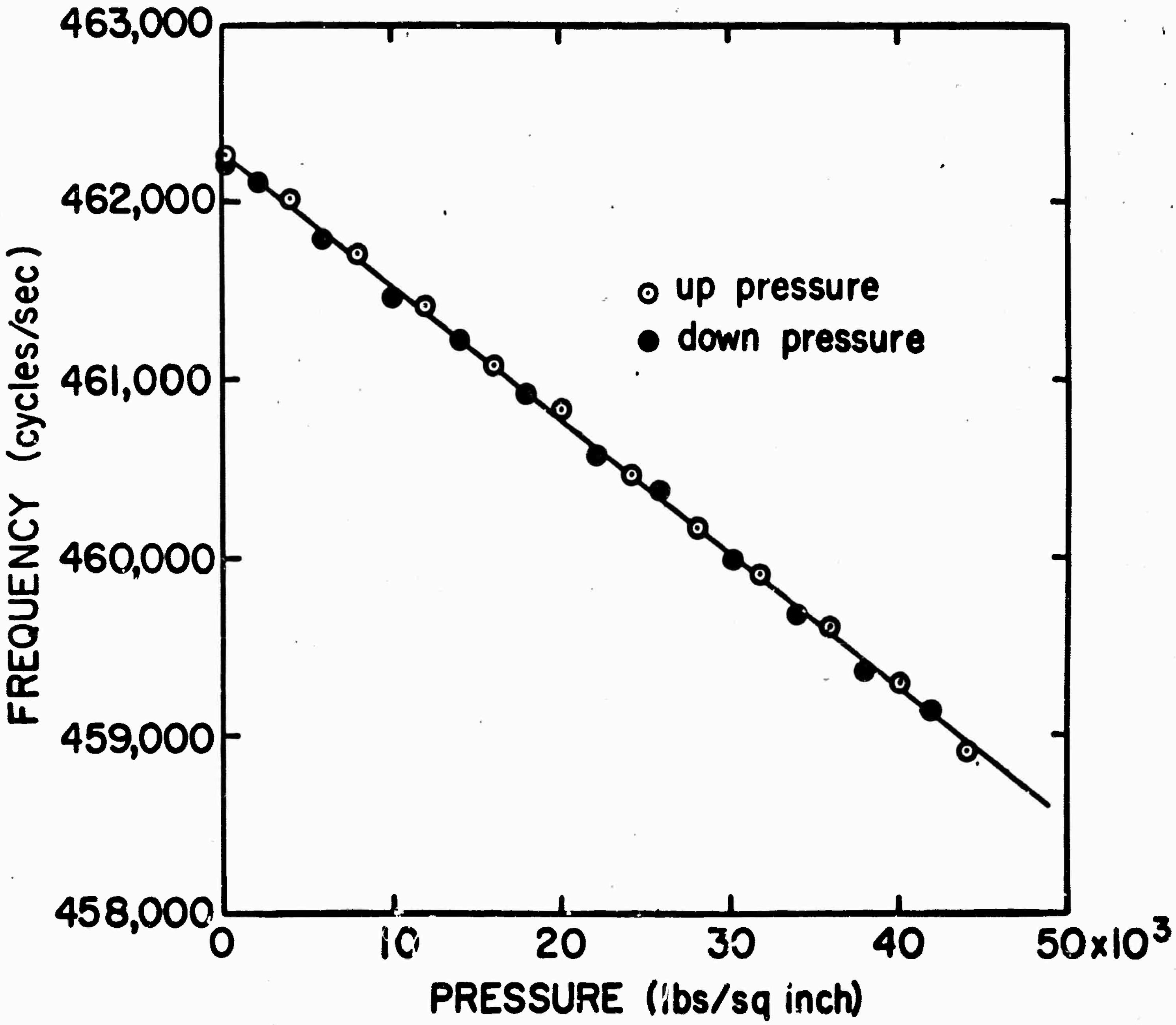
463,000
462,000
461,000
460,000
459,000
458,000
FREQUENCY (cycles/sec)
o up pressure
● down pressure
0
10
20
30
40
50x10³
PRESSURE (lbs/sq inch)

Fig.2

APPENDIX A

Pressure Derivatives of the Sound Velocities of Polycrystalline Forsterite, with 6% Porosity[1]

Edward Schreiber and Orson L. Anderson

Lamont Geological Observatory of Columbia University

Palisades, New York

The determination of the sound velocities of polycrystalline forsterite under pressure has been an important objective of our laboratory at Lamont. We have obtained numerous polycrystalline samples prepared in several laboratories and, until recently, have not been able to pass ultrasound through them. We finally obtained a sample of forsterite which yielded some weak echoes at 20 mHz, a barely marginal condition for measuring the elastic constants. We were able to determine the pressure derivatives of the sound velocities on this sample. The results should be of interest to the scientific community concerned with the physics of the earth's interior even though the results are on a porous sample, since they represent the only such data existing for forsterite. Indeed, it may prove quite difficult to obtain a sample which is both ideal and measurable with precise techniques.

Synthetic polycrystalline 'forsterite' was obtained in the form of a rod about 3/8" in diameter and 8' long.

---

[1]Lamont Geological Observatory Contribution No. 00`

The specimen was supplied by the Silk City Ceramic Company of Hawthorne, New Jersey. The density of this material was determined to be 3.021 or 94.0% of theoretical density. The specimen consists essentially of forsterite (95%) as determined by X-ray diffraction. A second phase present is probably barium aluminum silicate, but positive identification was not possible. The average grain size of the specimen is about 12 microns. In a thin section, the grains appear to be equidimensional with no apparent preferred orientation.

Examination of the polished surface as well as thin section indicated a porosity of 5 $\pm$ 1% consistent with the measured deviation of the density from the theoretical value, the pore structure consisting entirely of isolated pores, which was further verified during the density measurement. No gain in weight of the specimen was observed after it had been in boiling water for several hours. Most of the pores (>90%) are equidimensional and about 16-32 microns in diameter. Linear pores with moderate aspect ratios were observed. (The aspect ratio is a measure of pore elongation and is defined as the ratio of the pore width to pore length. The aspect ratio of a section through a sphere would be unity, and through a fine cleavage crack, near zero.) The aspect ratio of the pores found in this specimen was between 0.2 and 0.1.

According to Walsh [1965] and Brace [1965], the pressure required to close an elliptical cavity is given by

$$P = E\Theta \qquad (1)$$

where P is the pressure required to close the cavity, E is the Young's modulus of the material surrounding the cavity, and θ is the aspect ratio of the cavity. The value of the Young's modulus of olivine, based on the single crystal measurements of Verma [1960], is 2013 kb. If we take the aspect ratio of the elongated pores in the specimen to be 0.1, and if we assume the pores to be ellipsoids, 201 kb are required to close the pores. This is a very high pressure, indeed, and it would appear that the aspect ratio of the pores observed in the specimen is too large for pore closure to affect the measurement.

The velocities of both the longitudinal and shear wave disturbances were measured in a piece of the specimen 1.0444 cm in length at 25°C. The surfaces of the specimen were polished flat to 0.1λ of sodium light and parallel to 1×10^{-4} cm/cm. The method used to measure the velocities and their derivatives with pressure was pulse superposition [Schreiber and Anderson, 1966; McSkimin, 1961]. A carrier frequency of 10 mHz was used due to the high acoustic loss at 20 mHz. This is the first time that measurements with these precise techniques have been successfully obtained using so low a carrier frequency. The pressure-generating system has been previously described [Anderson and Schreiber, 1965].

The longitudinal and shear velocities of this specimen of forsterite, at 1 atm and 25°C (ambient pressure and tempera-

ture), were found to be

$$v_p = 7.587 \pm 0.25\%; \quad v_s = 4.359 \pm 0.25\% \text{ km/sec} \qquad (2)$$

The adiabatic moduli and Poisson's ratio were calculated using these velocities and the measured bulk density of 3.021 gm/cm^3 (see Table 1).

Verma [1960] determined the elastic constants for an olivine (density = 3.324). The Voigt-Reuss-Hill averaging scheme applied to his data yields a bulk modulus of 1313 kilobars. Using the method of Walsh et al. [1965] to adjust for the density difference between specimens, the two values of the bulk modulus agree to within 10%. The difference is no doubt due to compositional variation between the specimens.

Typical data for the variation of frequency with pressure are shown in Figures 1 and 2. As a result of the scatter, the slopes are known to about ± 5%.

Pressure variations of velocity and of the moduli were computed from the data as previously described [Schreiber and Anderson, 1966]. The variations of the longitudinal and shear mode velocities with pressure are given by equation (3), where P is in kilobars.

$$\begin{aligned} v_p &= 7.586 + 1.03 \pm 5\% \times 10^{-2} P \\ v_s &= 4.359 + 2.45 \pm 5\% \times 10^{-2} P \end{aligned} \qquad (3)$$

These data were used to evaluate the pressure derivatives of both the bulk modulus and of Poisson's ratio. These are $(dB_s/dP) = 4.8 \pm 0.5$ and $(d\sigma/dT) = 7.4 \pm 0.8 \times 10^{-4}$. The error in these derivatives arises principally from the error in slope of the velocity-pressure data.

The value of the Grüneisen constant $\gamma = 0.97$, for this sample, was calculated with the expression

$$\gamma = \frac{\alpha_v B_s}{\rho C_p} \tag{4}$$

and the isothermal bulk modulus computed to be 966.6 kb by

$$B_s/B_T = (1 + T\alpha_v\gamma) \tag{5}$$

The heat capacity $C_p = 7.889 \times 10^6$ dyne-cm/$^\circ$C/gm was obtained from Kubaschewski and Evans [1958], and the coefficient of volume expansion of this specimen $\alpha_v = 24 \times 10^{-6}\ ^\circ C^{-1}$ from Soga and Anderson [1966]. The value of γ would be about 20% higher for a nonporous sample due to the larger value of B_s at zero porosity.

The results of the present study are summarized for polycrystalline forsterite with 6% porosity in Table 1.

We are aware of the strong anisotropy exhibited by olivine in rock samples. We, therefore, checked our specimen for indications of anisotropy in two ways. First, a thin section was prepared and examined under crossed Nicol prisms with a polarizing microscope. Second, we measured the shear sound veloc-

ities, changing the orientation of the vibration direction. In both instances, the specimen was isotropic in its behavior.

The effect of pore closure on the velocity was not expected to present any problem in this case due to the pore geometry. The fact that the frequency pressure dependence is linear is evidence in support of this view. When cracks are closing, the velocity shows a very large nonlinear relation to pressure (for example, see Birch [1961]). We believe that the effect of porosity on the pressure derivative is not large, and that the values for the pore-free material will fall within the experimental limits reported here.

Acknowledgments. The writers thank N. Soga for his data on temperature effects on forsterite prior to publication.

This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR contract number AF-49(638)-1355.

REFERENCES

Anderson, O. L., and E. Schreiber, The pressure derivatives of the sound velocities of polycrystalline magnesia, J. Geophys. Res., 70(20), 5241-5248, 1965.

Brace, W. F., Some new measurements of linear compressibility of rocks, J. Geophys. Res., 70(2), 391-398, 1965.

Birch, F., The velocity of compressional waves in rocks to 10 kilobars, Part 2, J. Geophys. Res., 66(7), 2199-2224, 1961.

Kubaschewski, O., and E. L. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York, 1958.

McSkimin, H. J., Pulse superposition method for measuring ultrasonic wave velocities in solids, J. Acoust. Soc. Am., 33(1), 12-16, 1961.

Schreiber, E., and O. L. Anderson, Pressure derivatives of the sound velocities of polycrystalline alumina, J. Am. Ceram. Soc., 49(4), 184-190, 1966.

Soga, N., and O. L. Anderson, High temperature elastic properties of two magnesium silicate compounds, to be published.

Verma, R. K., Elasticity of some high-density crystals, J. Geophys. Res., 65(2), 757-766, 1960.

Walsh, J. B., The effect of cracks on the compressibility of rock, J. Geophys. Res., 70(2), 381-390, 1965.

Walsh, J. B., W. F. Brace, and A. W. England, Effect of porosity on compressibility of glass, J. Am. Ceram. Soc., 48(12), 605-608, 1965.

TABLE 1. Properties of Polycrystalline Forsterite with 6% Porosity

Property		Value	Units
Density	ρ	3.021	gm/cm^3
Long. Velocity	v_p	7.586	km/sec
Shear Velocity	v_s	4.359	km/sec
Bulk Modulus	B_s	973.6	kbar
Poisson's Ratio	σ	0.254	---
Pressure Deriv.Long.Velocity	$(\partial v_p/\partial P)_T$	1.03×10^{-2}	km/sec/kb
Pressure Deriv.Shear Velocity	$(\partial v_s/\partial P)_T$	2.45×10^{-2}	km/sec/kb
Pressure Deriv. Bulk Modulus	$(\partial B_s/\partial P)_T$	4.8	---
Pressure Deriv.Poisson's Ratio	$(\partial \sigma/\partial P)_T$	7.4×10^{-4}	kb^{-1}

FIGURE CAPTIONS

FIG. 1 Frequency versus pressure: Longitudinal mode in Mg_2SiO_4.

FIG. 2 Frequency versus pressure: Shear mode in Mg_2SiO_4.

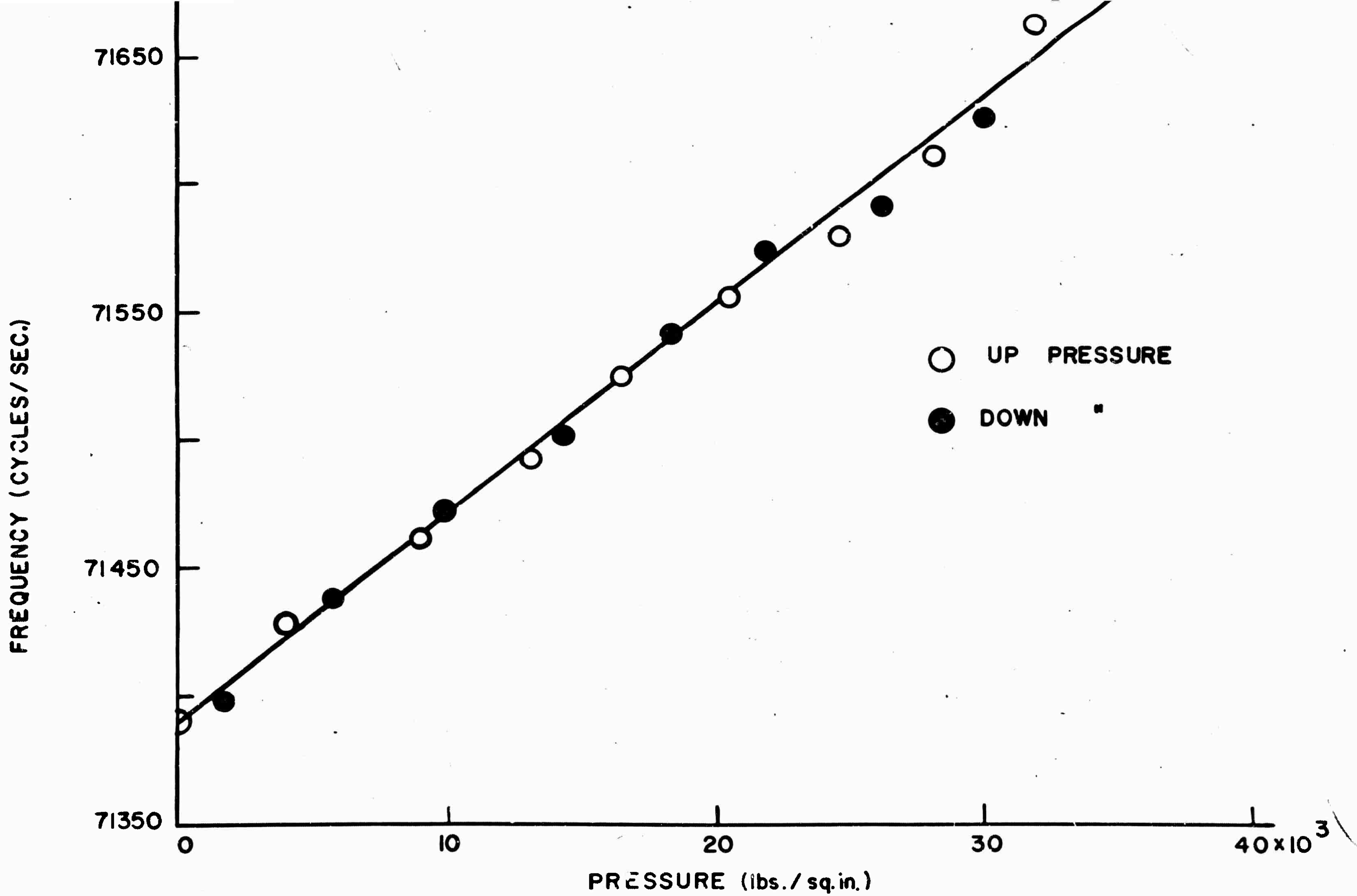
71650
71550
71450
71350
FREQUENCY (CYCLES/SEC.)
0
10
20
30
40x10^3
PRESSURE (lbs./sq.in.)
UP PRESSURE
DOWN "

Fig. 1

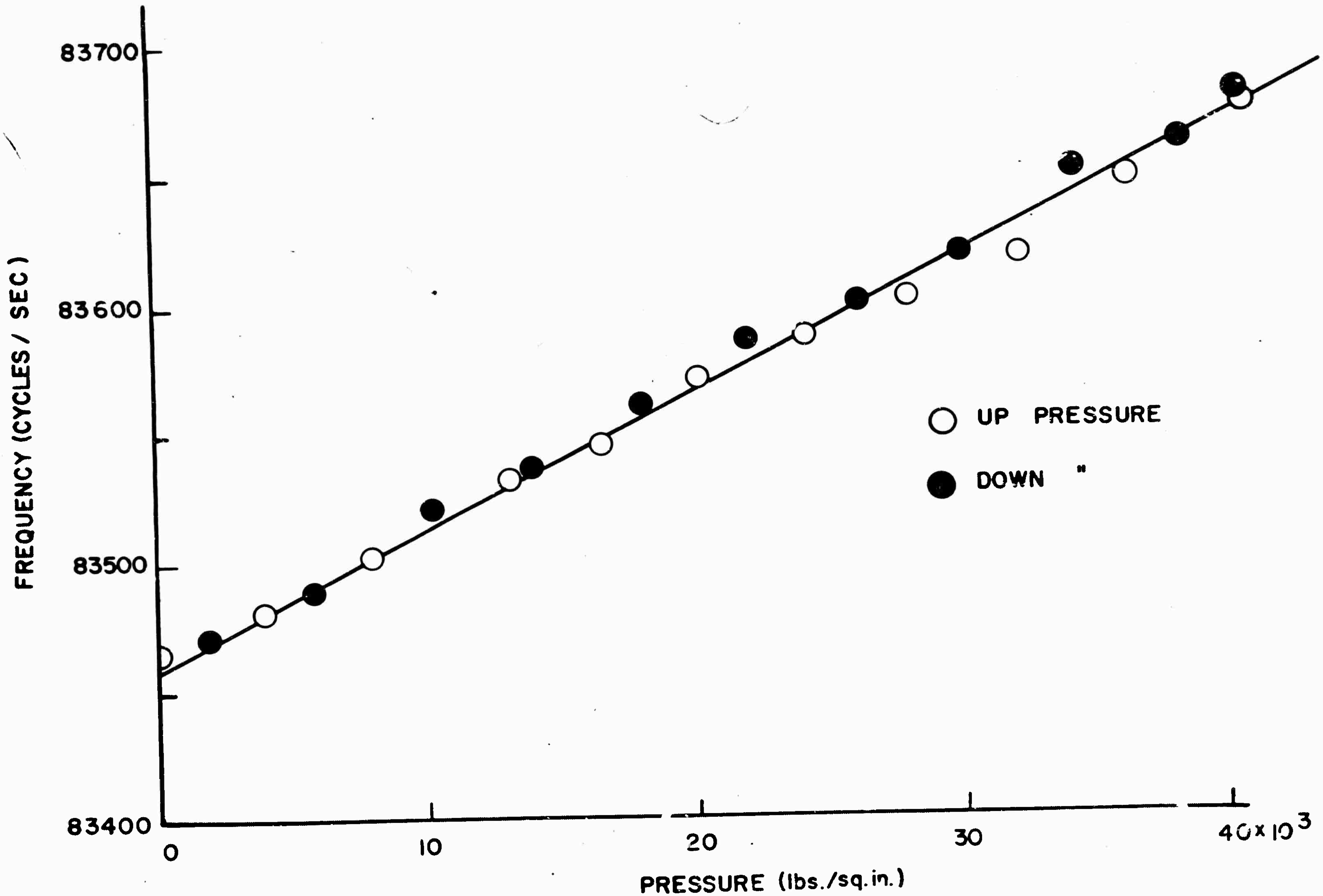
83700
83600
83500
83400
FREQUENCY (CYCLES / SEC)
0
10
20
30
40x10^3
PRESSURE (lbs./sq.in.)
UP PRESSURE
DOWN "

Fig.2

APPENDIX B

Elastic Moduli of Single Crystal Spinel at 25°C and to 2 Kbar

Edward Schreiber

Lamont Geological Observatory of Columbia University[1]

Palisades, New York

ABSTRACT

The elastic properties of a synthetic single crystal spinel with a composition of $MgO \cdot 2.6\ Al_2O_3$ have been determined at 25°C and up to 2 kbar by measuring propagational velocitites of ultrasonic waves using the method of pulse superposition. The isotropic moduli and Poisson's ratio were computed from the single crystal values using the Voigt-Reuss-Hill approximation.

Values of the elastic moduli at 1 bar and 2 kbar and at 25°C are

	c_{11}	c_{12}	c_{44}	
1 bar	2985.7	1537.2	1575.8	(kbar)
2 kbar	2995.5	1545.0	1577.5	(kbar)

The bulk modulus was computed to be 2019.9 kbar, and the pressure derivative of the bulk modulus was found to be 4.18.

---

[1]Lamont Geological Observatory Contribution No. 000

I. INTRODUCTION

The purpose of this communication is to present elastic moduli measurements made upon a specimen of synthetic single crystal spinel at 25°C from 1 bar to 2 kbar, and the application of these data to calculate the pressure derivatives of the elastic moduli and associated bulk properties.[1] Since elastic moduli data for both MgO and Al_2O_3 are available,[2,3] similar data for spinel are of interest. The spinel for which data are reported here has the formula $MgO \cdot 2.61\ Al_2O_3$. The value of the pressure derivative of the bulk modulus, dB/dP, is a significant parameter in evaluating equations of state. It has been shown that the value of dB/dP measured at low pressure allows one to estimate volume at very high pressure.[4]

II. MEASUREMENT

A single crystal spinel boule grown by flame fusion was obtained from the Commercial Mineral Corporation of New York City. The density of a specimen cut from this sample was measured by a volume displacement method, taking into account all buoyancy and surface tension corrections, and found to be $3.6193 \pm 2\times10^{-4}$ gms/cm^3. This value is 1% greater than the X-ray density calculated using the data of the N.B.S. for spinel[5] ($MgAl_2O_4$) prepared by sintering a stoichiometric mixture of the pure component oxides. A chemical analysis of this specimen indicated a composition of $MgO \cdot 2.61\ Al_2O_3$. Since it is possible that Al_2O_3 is soluble in

the spinel structure, thereby raising the density of the spinel phase (Clark *et al.*[6], Roy *et al.*[7]) an X-ray pattern was obtained with our specimen which indicated that only a spinel phase was present with a lattice spacing of 7.98Å. This spacing corresponds to a composition[6,7] of $MgO \cdot 2.6\ Al_2O_3$ and is in agreement with the results obtained from the chemical analysis.

The specimen, cut into an oriented cube with four (110) faces and two (100) faces, was polished flat to within 0.1λ of sodium light and the faces parallel to $1 \cdot x10^{-4}$ in/in. The crystallographic orientations were determined and maintained by X-ray methods. The elastic constants were determined by measuring the propagation velocity of ultrasonic waves through the crystal, employing the interferometric technique of pulse superposition.[8,9] This method has the concurrent advantages of high accuracy (0.01%) in measuring the absolute velocities and great sensitivity for detecting the small changes of velocity with pressure. This particular technique of measurement has been described[8,9,3] and will only be briefly outlined.

The output from a pulsed oscillator (tone burst) is applied to an appropriate quartz transducer which is bonded directly to the specimen. The frequency of the carrier wave in the tone burst is the same as the transducer resonant frequency, and the repetition rate of the tone burst is varied until its period is equal to the round trip delay time within the specimen. Under these circumstances, the transmitted and received pulses overlap, so the trans-

mitter is gated in order to view the returning echo pattern on an oscilloscope. The echoes are made to overlap and, by adjustment of the repetition rate, are made to interfere constructively. At the condition of constructive interference, the following equation applies[8,9]

$$t = 1/F + \phi/2\pi f - n/f \qquad (1)$$

where t is the round trip travel time of the wave within the specimen, F is the repetition rate of the applied signal, f is the carrier-wave frequency (40 mHz), ϕ a phase shift introduced at the transducer-bond interface, and n the integral number of cycles of displacement of the carrier wave in overlapping echoes. As the pressure is varied, the phase shift is maintained constant by adjusting the carrier frequency to the transducer resonance as it changes with pressure; thus the primary measurement is the repetition frequency F. The variation of the elastic moduli with pressure is determined by measuring the change in the repetition rate, and the velocity of a particular vibrational mode is calculated with the relation

$$v_i = v_{oi}\ (F/F_{oi})\ \ (\ell/\ell_o) \qquad (2)$$

where the zero subscripts refer to the ambient conditions of 25°C and 1 bar. The length ratio (ℓ/ℓ_0) is calculated from the frequency ratios following the method described by Cook.[10] For crystals of the isometric system, the length ratio is independent

of crystal orientation.

As shown by Mason,[11] the elastic moduli may be determined from the velocity measurements in the 100 and 110 crystallographic directions. In Table I, these velocities are listed and their relations to the three independent elastic moduli are indicated. Since there are three independent elastic moduli, only three velocities need be measured to completely define the system, but two extra velocities are measured for the purpose of a cross-check.

TABLE I. Relation of measured velocities to the elastic moduli.

Propagation Direction	Velocity and Vibration Direction	Formulae for Velocities
[100]	1 - v_ℓ [100]	$(c_{11}/\rho)^{1/2}$
	2 - v_s [110]	$(c_{44}/\rho)^{1/2}$
[110]	3 - v_ℓ [110]	$\left[(c_{11}+c_{12}+2c_{44})/2\rho\right]^{1/2}$
	4 - v_s [110]	$\left[(c_{11}-c_{12})/2\rho\right]^{1/2}$
	5 - v_s [100]	$(c_{44}/\rho)^{1/2}$

The pressure system employed has been described in Schreiber and Anderson[3] and is so designed that pressure and temperature are both measured in situ. A pressure balance is employed in order that the precision of the pressure measurement be consonant with the precision of the velocity measurement. The vessel tem-

perature is maintained at 25°C by circulating thermostated water through a copper coil surrounding the vessel. All measurements were performed within ±0.05°C of 25°C and with the piston of the pressure balance floating.

III. RESULTS AND DISCUSSION

A. Measurements at 1 bar

The results of the measurement of the wave velocities at the ambient conditions of 25°C and 1 bar are given in Table II. Verma[12] measured the velocities in a single crystal spinel and his results are included. Although the composition of his spinel is reported to be $MgO \cdot 3.5\ Al_2O_3$, there is close agreement between the two sets of velocities. It would appear that substitution of Al^{3+} for Mg^{2+} in the spinel lattice does not have any great effect on the velocities.

TABLE II. Measured wave velocities in spinel at 1 bar.

Designation	Velocity (km/sec) This Work*	Verma*
v_1	9.0833	9.10
v_2	6.5983	6.61
v_3	10.[illegible]6	10.30
v_4	4.4733	
v_5	6.5978	

*Densities are 3.63 gm/cm³ for Verma's specimen and 3.6193 gm/cm³ for the specimen reported here.

The elastic moduli computed from the measured density and velocities are given in Table III. The moduli are computed from different combinations of the wave velocities in order to cross-check the measurements. The compliances are computed from the average value for the corresponding moduli. The isotropic bulk (B) and shear (G) moduli are calculated from the single crystal values according to the well-known schemes of Voigt (for moduli) and Reuss (for compliances) and are finally reported as the averaged Voigt-Reuss-Hill value following Anderson.[1]

B. Measurements under Pressure

The change in repetition frequency with pressure is shown in Fig. 1, where the frequency ratio is plotted as a function of pressure. The solid lines represent the least square fit to each set of experimental data. The frequency ratios may be expressed by the following relations (P is in kbars):

$$\begin{aligned} F_1/F_{01} &= 1.000\ 000 + 7.21 \times 10^{-4}\ P \\ F_2/F_{02} &= 1.000\ 000 + 2.13 \times 10^{-4}\ P \\ F_3/F_{03} &= 1.000\ 000 + 5.98 \times 10^{-4}\ P \\ F_4/F_{04} &= 1.000\ 000 + 2.64 \times 10^{-4}\ P \end{aligned} \qquad (3)$$

The results obtained from the pressure data are summarized in Table IV. The frequency ratios given by Eqs. (3) were used to determine the length ratio (following Cook[10]) and the density ratio was calculated from the initial density (3.6193 gm/cm^3) and the length ratio. The isotropic moduli were computed in the manner described. The pressure derivative of the bulk modulus

TABLE III. Elastic properties of spinel at 25°C and 1 bar.

Property	Relation	Value
c_{11}	ρv_1^2	2986.1 kbars
c_{11}	$\rho(v_3^2 + v_4^2 - v_5^2)$	2985.4 "
Average		2985.7 "
c_{12}	$\rho(v_3^2 - v_4^2 - v_5^2)$	1536.9 "
c_{12}	$\rho(v_1^2 - 2v_4^2)$	1537.6 "
Average		1537.2 "
c_{44}	ρv_2^2	1575.7 "
c_{44}	ρv_5^2	1575.8 "
Average		1575.8 "
s_{11}	$(c_{11}+c_{12})/(c_{11}-c_{12})(c_{11}+2c_{12})$	5.1525×10^{-4} kbars^{-1}
s_{12}	$-c_{12}/(c_{11}-c_{12})(c_{11}+2c_{12})$	-1.7511×10^{-4} "
s_{44}	$1/c_{44}$	6.3467×10^{-4} "
B_v	$1/3(c_{11}+2c_{12})$	2020.0 kbars
G_v	$1/5(c_{11}-c_{12}+3c_{44})$	1235.0 "
B_r	$\left[3(s_{11}+2s_{12})\right]^{-1}$	2019.8 "
G_r	$\left[4/5(s_{11}-s_{12})+3/5s_{44}\right]^{-1}$	1071.7 "
B_{vrh}	$1/2(B_v+B_r)$	2019.9 "
G_{vrh}	$1/2(G_v+G_r)$	1153.3 "
σ	$(3B-2G)/2(3B+G)$	0.2601

TABLE IV. Summary of results for spinel at 25°C.

Length ratio at 2 kb (ℓ/ℓ_0) = 0.999664

Density ratio at 2 kb (ρ_0/ρ) = 1.001007

		1 bar	2 kb
Density (gm/cm^3)		3.6193	3.6229
Velocity (km/sec)	v_1	9.0[illegible]33	9.0934
	v_2	6.5983	6.5989
	v_3	10.296	10.305
	v_4	4.4733	4.4742
	v_5	6.5978	6.5984
Ave. Moduli (kbar)	c_{11}	2985.7	2995.5
	c_{12}	1537.2	1545.0
	c_{44}	1575.8	1577.5
Compliances (kbar^{-1})	s_{11}	5.1525×10^{-4}	5.1438×10^{-4}
	s_{12}	-1.7511×10^{-4}	-1.7503×10^{-4}
	s_{44}	6.3467×10^{-4}	6.3391×10^{-4}
Bulk Modulus (kbars)	B_v	2020.0	2028.5
	B_r	2019.8	2028.5
	B_{vrh}	2019.9	2028.5
Shear Modulus (kbars)	G_v	1235.0	1236.6
	G_r	1071.7	1073.1
	G_{vrh}	1153.3	1154.8
	σ	0.260	0.260

Pressure derivative bulk modulus

$(\Delta B/\Delta P)_T = 4.2$ $(dB/dP)_T = 4.18$

(dB/dP) was computed in two ways; first, as $(\Delta B/\Delta P)$ from the tabulated data which involve the approximate length change computation, and second, from the relation derived for the natural velocities by Thurston[13] and by Thurston and Brugger.[14] Their relation for crystals of cubic symmetry is

$$(dB/dP) = 2c_{11}(F_1/F_{01}) - 4/3(c_{11} - c_{12})(F_4/F_{04}) + 1/3(1+T\alpha\gamma) \quad (4)$$

Anderson[2] has pointed out that the latter represents computation by a slope whereas the former represents computation by a chord. The agreement between the two values, 4.20 and 4.18, obtained by the two methods of computation may be taken as evidence for the linearity of the bulk modulus pressure relationship.

It is useful to compute the bulk elastic properties as isothermal values for two reasons. First, it is the isothermal value which is obtained in experiments involving static compression; second, equations of state used to predict pressure volume relationships at high pressures ordinarily involve the isothermal value of B and of (dB/dP). The equation for the conversion is

$$B_T = B(1 + T\alpha\gamma)^{-1}$$
$$B_T = 1999 \text{ kbar} \quad (5)$$

where the T subscript denotes the isothermal value, T is the absolute temperature, α the coefficient of volume expansion, and γ the Grüneisen constant, which may be computed from

$$\gamma = \frac{B\alpha}{C_p\rho} \quad (6)$$
$$\gamma = 1.53$$

where C_p is the heat capacity at constant pressure and ρ the density. For the pressure derivative of the bulk modulus, the relationship is somewhat more involved and is given by (after Overton[15])

$$dB_T/dP)_T = (dB/dP)_T + \left[T\alpha\left(B_T/B\right)\right]\left[(-2/\alpha B_T)(dB/dT)_p - 2(dB/dP)_T\right] + \left[T\alpha\left(B_T/B\right)\right]^2\left[(dB/dP)_T - (1/\alpha^2)(d\alpha/dT)_p - 1\right] \quad (7)$$

$(dB_T/dP)_T = 4.19$

The values used in evaluating the isothermal properties from the adiabatic at $T = 298^{\circ}K$ are: $\rho = 3.6193\ g/cm^3$ and $B = 2019.9$ kbar (this work), $\alpha = 22.5\times10^{-6}\ {}^{\circ}C^{-1}$, and $d\alpha/dT$ 5×10^{-8} (Skinner[16]), $C_p = 27.8 cal\text{-}deg^{-1}\text{-}mol^{-1}$ (Kubaschewski and Evans[17]), and (dB_T/dT) was estimated to be $-0.21\ kb^{\circ}C$ from the work reported by Soga _et al._[18]

Anderson[4] has shown that for the condition where the bulk modulus is linear with pressure the Murnaghan equation of state integrates to (V is volume)

$$\ln(V_o/V) = \left[1/(dB_T/dP)_T\right]\ln\left[(dB_T/dP)_T(P/B_T) + 1\right] \quad (8)$$

which contains no arbitrary constants and he has demonstrated the applicability of Eq. (8) to numerous compounds. The agreement between the two methods of computing (dB/dP), shown in Table IV, indicates that B_T is linear with pressure and therefore Eq. (8) should apply for spinel. In this case, the equation of state

for spinel is

$$\frac{V_o}{V} = \left[2.06\mathrm{x}10^{-3}\ P + 1 \right]^{0.239} \qquad (9)$$

Equation (9) should hold up to at least 1000 kbars if there is no phase change.[4]

ACKNOWLEDGMENTS

The author wishes to thank Dr. O. L. Anderson for his advice and encouragement.

This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR contract number AF-49(638)-1355.

The author also wishes to gratefully acknowledge support from NSF Grant GP 4437 received during the course of this work.

REFERENCES

[1]Anderson, O. L., "A Simplified Method for Calculating the Debye Temperature from Elastic Constants," J. Phys. Chem. Solids, 24, 909-917 (1963).

[2]Anderson, O. L., and P. Andreatch, "The Pressure Derivatives of the Elastic Constants of Single Crystal MgO at 25°C and -195.8°C," J. Am. Ceram. Soc., 48(8), 404-409 (1966).

[3]Schreiber, E., and O. L. Anderson, "Pressure Derivatives of the Sound Velocities of Polycrystalline Alumina," J. Am. Ceram. Soc., 49(4), 184-190 (1966).

[4]Anderson, O. L., "The Use of Ultrasonic Measurements under Modest Pressure to Estimate Compression at High Pressure," J. Phys. Chem. Solids, 27, 547-565 (1966).

[5]Swanson, H. E., and R. K. Fuyat, "Standard X-ray Diffraction Powder Patterns, N.B.S. Circular 539, Vol. II (1953).

[6]Clark, G. L., E. L. Howe, and A. L. Badger, "Lattice Dimensions of Some Solid Solutions in the System $MgO-Al_2O_3$," J. Am. Ceram. Soc., 17, 7-8 (1934).

[7]Roy, D. M., R. Roy, and E. F. Osborn, "The System $MgO-Al_2O_3-H_2O$ and Influence of Carbonate and Nitrate Ions on Phase Equilibria," Am. J. Sci., 251, 337-361 (1953).

[8]McSkimin, H. J., "Pulse Superposition Method for Measuring Ultrasonic Waves in Solids," J. Acoust. Soc. Am., 33, 12-16 (1961).

[9]McSkimin, H. J., and P. Andreatch, "Analysis of the Pulse Superposition Method for Measuring Ultrasonic Wave Velocities as a Function of Temperature and Pressure," J. Acoust. Soc. Am., 34(5), 609-615 (1962).

[10]Cook, R. K., "Variation of Elastic Constants and Static Strains with Hydrostatic Pressure; A Method for Calculation from Ultrasonic Measurements," J. Acoust. Soc. Am., 29(4), 445-448 (1957).

[11]Mason, W. P., American Institute of Physics Handbook, (McGraw-Hill Book Company, New York, 1957), 2nd ed., Ch. 3f.

[12]Verma, R. K., "Elasticity of Some High Density Crystals," J. Geophys. Res., 65(2), 757-766 (1960).

[13]Thurston, R. N., "Ultrasonic Data and the Thermodynamics of Solids," IRE Proc. 53, (October 1965).

[14]Thurston, R. N., and K. Brugger, "Third Order Elastic Constants and the Velocity of Small Amplitude Elastic Waves in Homogeneously Stressed Media," Phys. Rev., 133, A 1604-1612 (1964).

[15]Overton, Jr., W. C., "Relation between Ultrasonically Measured Properties and the Coefficients in the Solid Equations of State," J. Chem. Phys., 37(1), 116-119 (1962).

[16]Skinner, B. J., "Thermal Expansion," in Handbook of Physical Constants, section 6, S. Clark, Ed., Geol. Soc. Am., Memoir 97, New York (1966).

[17]Kubaschewski, O., and E. L. L. Evans, Metallurgical Thermochemistry, 3rd ed., (Pergamon Press, New York, 1958).

[18]Soga, N., E. Schreiber, and O. L. Anderson, "Estimation of Bulk Modulus and Sound Velocities of Oxides at Very High Temperatures," J. Geophys. Res., 71(22), 5315-7320 (1966).

FIGURE CAPTION

Fig. 1 Variation of frequency ratio with pressure.

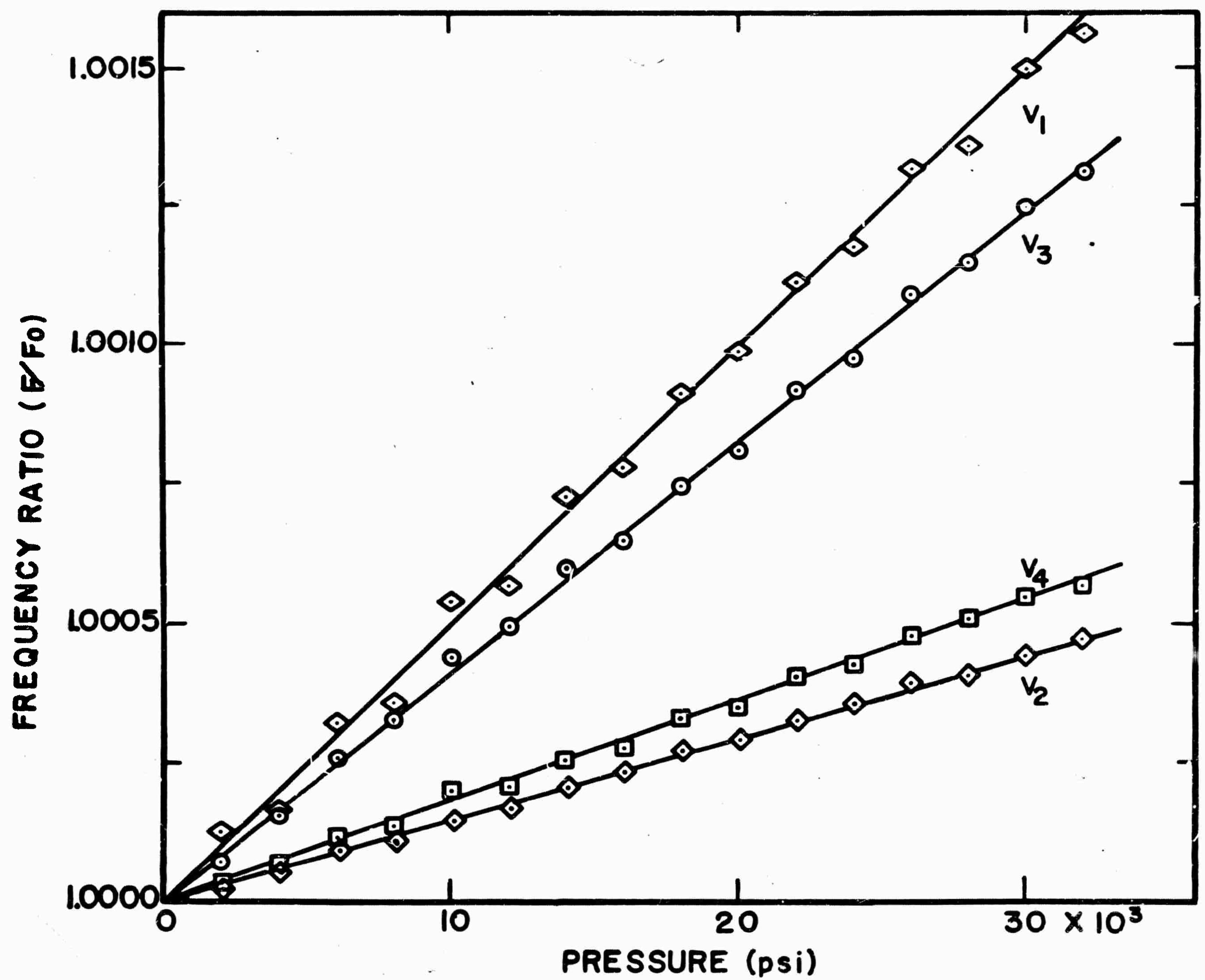
FREQUENCY RATIO (F/Fo)
1.0015
1.0010
1.0005
1.0000
0
10
20
30 X 10³
PRESSURE (psi)
ν_1
ν_3
ν_4
ν_2

Fig. 1